

A11101 947069

NAT'L INST OF STANDARDS & TECH R.I.C.



A11101947069

/Bureau of Standards Journal of research

QC1 .U52 V5:183-258:1930 C.2 NBS-PUB-Q1

[illegible]

PRINTED IN U.S.A.

APPARATUS FOR THE DETERMINATION ABOARD SHIP OF THE SALINITY OF SEA WATER BY THE ELECTRICAL CONDUCTIVITY METHOD

By Frank Wenner, Edward H. Smith, and Floyd M. Soule¹

ABSTRACT

The apparatus described furnishes a convenient means for the determination of the salinity of samples of sea water as they may be collected. It consists essentially of a Wheatstone bridge, conductivity cells of a type which may be filled and emptied during fairly rough weather, and the necessary auxiliary equipment, all built into a single cabinet.

A special feature is the use of two similar conductivity cells in adjacent arms of the bridge. When both are filled with samples of sea water, even though not of the same salinity, both have very nearly the same temperature coefficient, so the balance of the bridge is not greatly affected by small uncertainties of the temperature. Further, the complicated actions taking place at the electrodes, generally referred to as polarization, are substantially the same in both cells, so the effects of polarization are largely neutralized.

A further special feature, not really a part of the equipment but of a plan for its use, is that a supply of standard sea water or sea water of which the salinity has been determined by laboratory methods is carried aboard and used for periodic standardizations. Samples of sea water to be tested, together with a sample of standard sea water, are substituted one after another in the same conductivity cell. This gives a direct comparison of the sample of unknown salinity with that of a standard, almost if not quite independent of the cell constant, largely independent of other constants of the equipment and largely independent of systematic errors.

Apparatus of the type has been used during the past several seasons in the International Ice Patrol Service, also on the *Marion* expedition and on the last cruise of the nonmagnetic vessel *Carnegie*.

CONTENTS

	Page
I. Introduction.....	711
II. Method of measurement.....	713
III. Circuits.....	714
IV. Coast Guard equipment.....	715
1. Description.....	715
2. Calibration.....	718
3. Procedure in use.....	721
V. Carnegie Institution equipment.....	723
1. Description.....	723
2. Calibration.....	724
2. Discussion of temperature coefficient.....	728
VI. Recommended changes in construction.....	729
VII. Summary.....	732

I. INTRODUCTION

No doubt the idea of determining the salinity of sea water from measurements of its electrical conductivity has occurred to many. Some of the attempts made during the years 1914 to 1921, inclusive, to perfect apparatus for this purpose are described in Bulletin No. 9

¹ Frank Wenner, National Bureau of Standards; Edward H. Smith, United States Coast Guard; and Floyd M. Soule, Carnegie Institution of Washington.

of the United States Coast Guard entitled "Ice Observations and Ice Patrol Service for the Season 1921." Much of this earlier work was done by A. L. Thuras, a part while he was connected with the National Bureau of Standards and a part while he was scientific observer in the Ice Patrol Service.

To give satisfactory results the apparatus should be capable of reproducing measurements of the electrical conductivity to 1 part in 4,000, corresponding roughly to changes of 10 mg per liter total salt and something less than 1 part in 100,000 in the density. This could be obtained readily in the laboratory, but the conditions at sea are such as to make the problem much more difficult. For convenience in use, the equipment should be relatively small in size and constitute a unit rather than an assemblage of a number of pieces of apparatus. Further, it should be capable of being operated from the lighting circuit of the ship on which it is installed. The equipment must be sufficiently rugged or so protected as not to suffer mechanical injury during the severest storms, and should be capable of being used during rough weather. The electrical insulation must remain good in the presence of an ocean atmosphere, and should not be injured in case sea water is spilled over parts of the apparatus. As the temperature coefficient of the electrical conductivity of sea water is in the neighborhood of 2 or 3 per cent per ° C., to obtain a precision of 1 part in 4,000 the temperature must be controlled to better than one-hundredth ° C. or provision made to compensate for uncertainties of the temperature. Also the various manipulations necessary in making measurements should be the simplest possible consistent with obtaining the precision sought.

The first apparatus intended to fill these requirements was designed by Wenner in 1922, and constructed in the Bureau of Standards during the latter part of 1922 and the early part of 1923. The original calibration was based on measured constants of the apparatus and the data concerning the electrical conductivity of sea water obtained in the earlier investigations referred to above. This apparatus was installed in the United States Coast Guard cutter *Tampa* just before the beginning of the 1923 International Ice Patrol Service, when the first attempts to use it were made by Smith, then scientific observer. Between the 1923 and 1924 ice-patrol seasons Smith made a rather complete calibration of the instrument using titrated samples of sea water. A description intended primarily for the information of those whose duty it might be to use the apparatus is given in Bulletin No. 12 of the United States Coast Guard, entitled "International Ice Observations and Ice Patrol Service Season 1924." Since then two additional equipments have been constructed, one on contract for the Coast Guard, which will be referred to as the second equipment, and one by the Department of Terrestrial Magnetism of the Carnegie Institution of Washington, which will be referred to as the third equipment, or the Carnegie Institution equipment. Since the second equipment for the Coast Guard was completed both the first and second have been used in the Ice Patrol Service, excepting the past two seasons when only one was available, the other having been destroyed by fire while in storage between seasons. Also one equipment was used on the *Marion* expedition into Baffin Bay during the summer of 1928. Some reference to the results obtained in the use of the first two equipments will be found in re-

ports of the Coast Guard since 1924. The third equipment was installed on the nonmagnetic vessel *Carnegie* just prior to her departure on her Cruise VII. This equipment was used by Soule from the time of its installation in the spring of 1928 until the fall of 1929 when the cruise was terminated by the destruction of the vessel. Some idea of the performance of this equipment will be given in this paper, although the complete data collected will be published by the Carnegie Institution of Washington, along with the other results of the expedition, in the reports of the *Carnegie's* Cruise VII.

The reader must bear in mind that two of the three instruments built have been destroyed by fire and that the third is not at present available to the authors. Consequently this paper has been prepared from notes, laboratory data, photographs, field records, and memory. Therefore, there occur in the following pages, statements which are general where the authors would have preferred to give specific

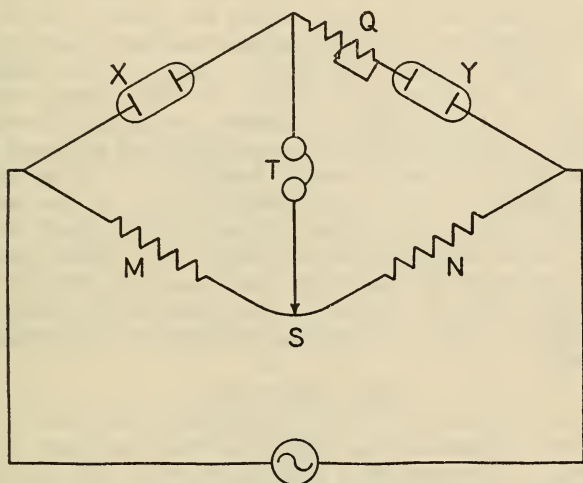


FIGURE 1.—Simplified diagram of electrical circuit

quantitative data. It is believed, however, that the lack of such specific data will neither keep the theory from being understood nor be a serious disadvantage in the design and construction of other such instruments.

II. METHOD OF MEASUREMENT

A simplified diagram of the electrical circuit is shown in Figure 1. Here *X* and *Y* represent two similar electrolytic cells, and also the resistance of these cells when filled with sea water. *Q* is an adjustable resistance in series with *Y*. *M* and *N* are fixed resistances, *S* is a slide wire, \sim represents the source of the alternating test current, and *T* is the telephone receiver for indicating a lack of balance of the bridge. A special feature is the use of two similar cells in adjacent arms of the bridge. When both cells are filled with sea water, even though the salinity of the sea water in one is not the same as that in the other, both have very nearly the same temperature-

coefficient. If, therefore, Q is small in comparison with Y , the differential temperature coefficient between X and $(Y+Q)$ will be small in comparison with that of the electrical conductivity temperature coefficient of the sea water in the X cell. As a consequence, the balance of the bridge is not greatly affected by small uncertainties of the temperature, provided both cells are very accurately at the same temperature. As in all bridge measurements the precision obtainable is limited among other factors by the heating produced by the test current. However, with this arrangement the test current raises the temperature of the sea water in both cells above that of the bath, in which the cells are located, by substantially the same amount since the thermal characteristics of the two cells are closely alike. Consequently a much larger test current may be used than would otherwise be permissible. Further, the complicated actions taking place at the electrodes, generally referred to as electrolytic polarization, will be substantially the same in both cells, so that the effects of polarization in one cell upon the balance of the bridge is largely neutralized by the effects of polarization in the other cell.

Another special feature not really a part of the bridges but a part of the plan for their use and kept in mind during the design is that a supply of Copenhagen standard sea water or sea water of known salinity or known density is carried aboard and used in periodic standardization of the equipment. Samples of the sea water to be tested, and samples of the standard sea water or sea water whose properties have been determined by laboratory methods, are substituted one after the other in the same cell. This gives a direct comparison between the unknown and standard samples almost if not quite independent of the cell constant, largely independent of other constants of the equipment, and largely independent of systematic errors.

III. CIRCUITS

A complete diagram of the bridge circuit is shown in Figure 2. Here W and P are two fixed resistances with the equivalent of a slide wire between them, and together they constitute the Wagner branch with the contact connected to the inclosing metallic shield G . The Wagner branch serves to bring the telephone receivers to the potential of the shield to which the observer is connected, and so forms a part during measurements. The switch or key R serves to connect one of the detector (telephone receiver) terminals of the bridge to the shield and this disturbs the balance of the bridge except when the Wagner branch is properly adjusted. This key is closed only during this adjustment. L is a mutual inductance between one of the leads from the source of the test current and the telephone leads. It serves to introduce into the telephone circuit a quadrature electromotive force so as to balance any of the out of phase components of potential difference in the bridge from whatever source they may arise, such as capacitance to ground, capacitance in the cells, polarization, etc. This mutual inductance is adjustable from a small negative through zero to a small positive value. To balance the bridge requires a proper setting of the slide wire contact or index, a proper setting of the mutual inductance, and a proper setting of the contact on the Wagner branch. As these three adjustments are not independent of each other, they must, in principle at least, be

made in successive approximations. However, if the slide wire first is set at a point giving a minimum sound in the telephones and this sound then reduced as much as possible first by an adjustment of the mutual inductance and then by an adjustment of the Wagner branch, these two adjustments usually will be sufficiently exact, so that the slide wire contact may then be adjusted with the required precision. Only in case the reading of the slide wire index corresponding to the second adjustment differs materially from that of the first, need additional adjustments of the mutual inductance or the Wagner branch be made. There is nothing to be gained by repeating either unless a third adjustment of the slide wire contact is made. The reading of the slide wire index for the adjustment made

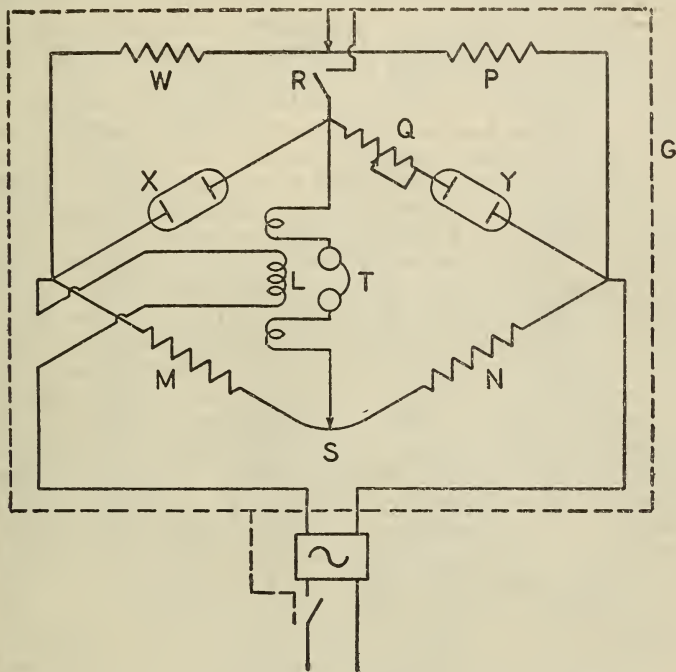


FIGURE 2.—Complete diagram of bridge circuit

after the adjustments of the mutual inductance and the Wagner branch is the only one which is significant. However, the final adjustment of the contact on the slide wire should not be made until a sufficient time after placing a sample of sea water in the *X* cell for the establishment of temperature equilibrium to well within 0.01°C .

IV. COAST GUARD EQUIPMENT

1. DESCRIPTION

A photograph of the second equipment is shown in Figure 3. Here the doors of the cabinet are removed to give an unobstructed view of the various parts. It will be seen that there are four compartments. The lower compartment on the right contains the bath in which the main part of two *X* and one *Y* cells, a thermoregulator,

a stirring propeller, and heating units are located. The upper compartment on the right contains the stirring motor, relay, air circulating fan, upper parts of the cells, thermoregulator heaters, the connections between the cells and the rest of the measuring circuit, and a lamp for keeping the compartment dry. The lower left compartment contains a microphone hummer for producing the alternating test current. This is packed in hair felt to prevent sound from it interfering with the detection of sound of the same pitch in the telephone receivers. The upper left compartment contains the major part of the measuring circuit, a lamp for keeping the compartment dry, the various switches and key, and the telephone receivers when not in use. Both upper compartments are metal lined except at their tops, and the arrangement is such that sea water, spilled in either can not get into either of the lower compartments. These linings and the metal walls of the bath are electrically connected and constitute the major portion of the shield *G*.

Conditions aboard ship are such as to make it impracticable to use an open bath or to handle cells except during favorable weather, consequently, the bath is tightly closed, though not hermetically sealed, and the cells are so designed that they may be emptied and refilled without being removed from the bath. A photograph of one of the cells is shown in Figure 4. The central portion of the cell is approximately 10 cm long and 1 cm internal diameter. The end bulbs containing the electrodes are approximately spherical and have a diameter of about 3 cm. When filled with sea water of average salinity, the resistance is in the neighborhood of 200 ohms. The electrodes are hollow truncated cones of platinum covered with platinum black. They are arranged so as to avoid undue concentration of the current in the sea water at their edges, and so as to avoid trapping air bubbles on their surface. From each electrode a platinum wire extends through an end bulb into a side tube which extends upward along the side of the cell. A quantity of mercury in each of these side tubes serves for connecting the cell into the bridge circuit. The cell is filled through the small funnel at the top and emptied by siphoning through the tube connected to the bottom of the lower terminal bulb and extending upward along the side of the cell. The cells are mounted in metal supports which terminate at their upper end in a ring, and this ring is clamped to the metal top of the bath. A rubber gasket between the ring and the top of the bath serves to make a water-tight connection. Inside this ring is a metal tube about 6 cm. in diameter and about 6 cm long. This tube is filled with wax, which constitutes the main part of the fastening between the cell and its metal support. The wax also serves for closing the bath so that sea water can not be spilled into it and to better insulate the cell from the metal shield.

The slide wire is of the Kohlrausch type having 10 turns and a resistance from 25 to 30 ohms. The exact value is not of much importance, and further can not conveniently be made to have an even value such, for example, as 25 ohms. The range of the slide-wire index extends from zero to 1,000 divisions and the wire within this range, or as much of it as will be used, should be fairly uniform. The slide wires used were made by the Leeds & Northrup Co., of Philadelphia. The resistance of the end coils *M* and *N* are made equal and of such magnitude that their combined resistance plus the resistance of the

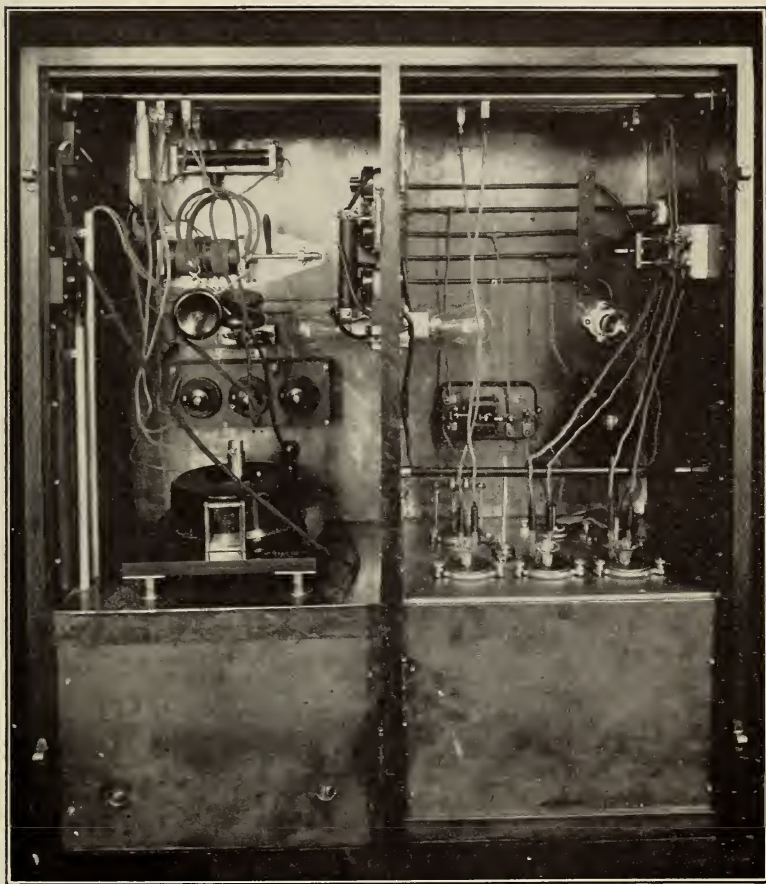


FIGURE 3.—*Second instrument for United States Coast Guard*



FIGURE 4.—*U n m o u n t e d*
electrolytic cell

slide wire is accurately 15,000 times the resistance per division of the slide wire as measured by the graduations of the head or frame which carries the contact. The end coils are metal covered, except at their lower end, and preferably hermetically sealed. Further, they are mounted in the upper part of the cabinet so there is little chance of sea water being spilled upon them, and little chance that they will be injured if such spilling occurs. The resistance of each of the fixed coils of the Wagner branch is in the neighborhood of 200 ohms, and that of the slide wire between them is about 40 ohms. Each telephone receiver has a resistance of about 10 ohms and a probable impedance at 1,000 cycles of the order of 100 ohms. The resistance Q is adjustable over a range of about 5 ohms in steps as small or smaller than 0.05 ohm. The contacts in Q have indices, so that after a change it can be reset to a former value.

The test current has a frequency of 1,000 cycles per second and is supplied by a microphone hummer made by the General Radio Co., of Cambridge, Mass. For the operation of this hummer a 6-volt

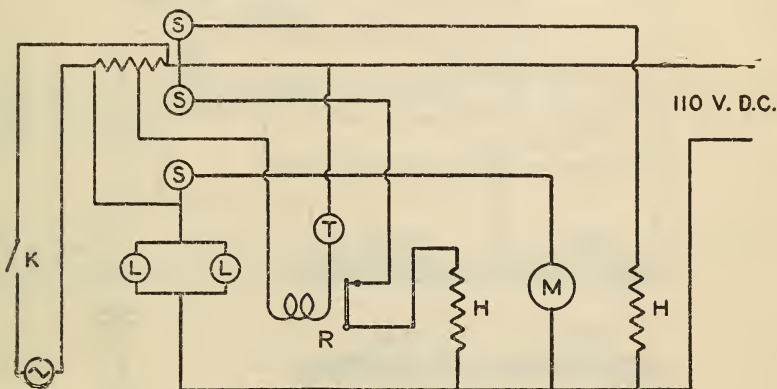


FIGURE 5.—Diagram of power circuit

direct-current source is required, also for the operation of a relay used in controlling the temperature 2 to 4 volts is required. To get these 2 low direct-current voltages from the direct current lighting circuit of from 100 to 120 volts, taps are made across a resistance connected in series with two lamps in parallel, each of about 50 watts. One of these lamps is located in each of the two upper compartments and serves to keep the inside of the cabinet at a temperature above the surrounding air. This elevated temperature is, or may be, of material assistance in maintaining the insulation of the measuring circuit. The lighting circuit of the ship also furnishes power for driving the motor which stirs the bath in which the cells are located, and for maintaining the bath at the desired temperature. A diagram of the power circuit is shown in Figure 5. Here S, S, S , represents switches; M , the motor for stirring the bath; H, H , heaters for keeping the bath at the desired temperature; T , thermoregulator; R , relay with armature contact in series with one of the bath heaters; L, L , lamps, one in each compartment, for keeping the upper compartments dry and substantially at the same temperature as the bath; and K is a switch or key in the power circuit to the hummer.

A diagram of the hummer circuit is shown in Figure 6. It should be noted that the hummer circuit is such that the measuring circuit is insulated from the circuit supplying power to the hummer; that is, the lighting circuit of the ship. At this point it should be mentioned that the key in the circuit supplying power to the hummer is of the spring type, normally open, and so arranged with respect to a small metal plate connected to the shield that when the key is held closed by the observer he almost of necessity is connected to and thus constitutes a part of the shield as stated above. The connection between the parts of the bridge circuit in the two upper compartments are made by horizontal metal tubes in the top of the cabinet, and these are well insulated. Also, other parts of the bridge circuit are arranged with a view of keeping the insulation high. Each winding of the mutual inductance between one of the leads supplying the test current and the telephone leads consists of approximately 50

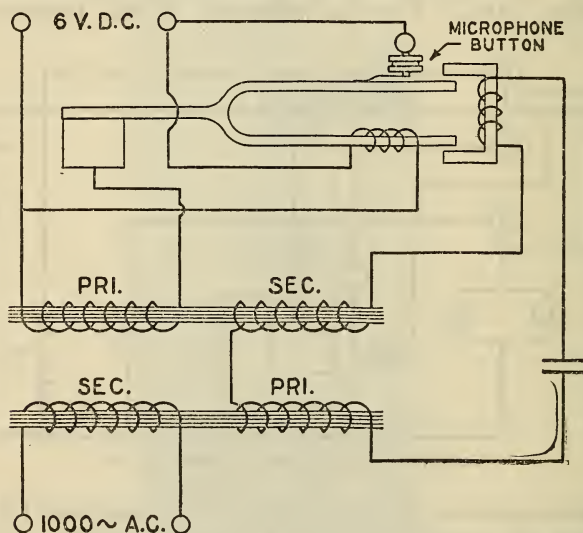


FIGURE 6.—Diagram of microphone hummer circuit

turns of insulated wire on tubes which telescope into each other. One of these windings is in two parts, one in each of the telephone leads; and these windings are differentially connected so that by sliding one tube with respect to the other the value of the mutual inductance can be changed continuously from a negative to a positive value. Between these two windings is the third winding, one end of which is connected to and thus forms part of the shield.

2. CALIBRATION

It can be shown that a second-degree equation should give a good approximation to the calibration curve for this type of instrument.

Consider the conditions where a solution of known salinity S' and of resistivity R' is placed in the cell X . Let X' be the resistance of the arm of the bridge including the cell X and let N and M be the resistances of the ratio arms with the slide wire set to some reading s' which corresponds to the salinity S' and let the bridge be balanced by

adjusting the resistance Q . Then if $(Q + Y)$ represents the resistance of the arm including Q we can write

$$X' = (M/N) (Q + Y) \quad (1)$$

If now the sea water in the measuring cell is replaced by a sample of higher salinity S and consequently lower resistivity R' and the bridge is balanced by increasing the slide-wire reading from s' to s , the resistance of the arm containing the measuring cell is given by the equation

$$X = \frac{M (1 - m (s - s'))}{N (1 + n (s - s'))} (Q + Y) \quad (2)$$

where m is the resistance of one division of the slide wire divided by M , and n is the resistance of one division of the slide wire divided by N . From equations (1) and (2) we have

$$X = X' \frac{(1 - m (s - s'))}{(1 + n (s - s'))} \quad (3)$$

Since the same cell has been used for the two samples, the ratio of resistivities of the two samples is the same as the ratio of the resistances, and hence

$$R = R' \frac{(1 - m (s - s'))}{(1 + n (s - s'))} \quad (4)$$

If C and C' represent conductivities; that is, the reciprocals of R and R' , respectively, equation (4) can be written

$$C = C' [1 + (n + m) (s - s') + (mn + m^2) (s - s')^2 + (m^2n + m^3) (s - s')^3 \dots] \quad (5)$$

The relation between electrical conductivity and salinity of sea water over the range 30 to 40 ‰ salinity can be closely approximated by the equation

$$C = C' (A + BS)$$

where A and B are constants and S is the salinity. Substituting this expression for C in equation (5) gives us

$$A + BS = 1 + (n + m) (s - s') + (mn + m^2) (s - s')^2 + (m^2n + m^3) (s - s')^3 \dots$$

or

$$S = \frac{1 - A}{B} + \frac{(n + m)}{B} (s - s') + \frac{(mn + m^2)}{B} (s - s')^2 + \frac{(m^2n + m^3)}{B} (s - s')^3 \dots$$

which can be written

$$S = S' \left[1 + \frac{(n + m)}{S' B} (s - s') + \frac{(mn + m^2)}{S' B} (s - s')^2 + \frac{(m^2n + m^3)}{S' B} (s - s')^3 \dots \right] \quad (6)$$

where S' is the salinity corresponding to the conductivity C' .

From the work of E. Ruppin² and A. L. Thuras³ mean values of the constants A and B give the relation that

$$C_s = C_{35} (0.10925 + 0.02545S)$$

where C_s is the conductivity at any salinity S ‰ and C_{35} is the conductivity at a salinity of 35 ‰ (‰ = parts per 1,000). With these values of A and B equation (6) can be written

$$S = 35 \left[1 + \frac{(n+m)}{0.89075}(s-s') + \frac{(mn+m^2)}{0.89075}(s-s')^2 + \frac{(m^2n+m^3)}{0.89075}(s-s')^3 \dots \right] \quad (7)$$

in which s' is the slide-wire reading corresponding to a salinity of 35 ‰. Inspection shows that, if, as was true of all the instruments so far built, one division of the slide wire represented 1/15,000 of the sum of the resistances of the ratio arms, all terms involving $(s-s')$ to exponents greater than 3 may be neglected, and that the third-degree term need only be considered when $(s-s')$ is numerically large.

Among the laboratory tests which should be made on an instrument of this sort is the test for uniformity of the slide wire. Differently stated, the corrections to the slide-wire reading as an indication of the ratio of the resistances of the two arms should be determined. Thus, if the resistance of one division of the slide wire is to be 1/15,000 the total resistance of the two arms, a slide-wire reading of 750 should occur when the ratio of the resistance of N to the resistance $(N+M)$ is 7,750/15,000. If actual test shows the ratio to be 7,753/15,000, the correction to be applied to the slide-wire reading at 750 is 3. A table of such corrections should be determined, at least for that part of the slide wire which is to be used.

Having tested the slide wire for uniformity and quantitatively determined its irregularities, it is then possible to construct a calibration curve or table for converting slide-wire readings into values of salinity from published data on the conductivity of sea water. This, as in all methods of calibrating such an instrument, involves the arbitrary selection of one point on the calibration curve.

A more satisfactory method of arriving at the values for a table for converting slide-wire readings into salinities would be the selection of one point on the curve and the determination by measurement of two other points. This involves the use of three samples of known and different salinities. The curve could then be closely approximated by drawing the curve of a second-degree equation through the three known points. Such a method would have the advantage of eliminating uncertainties regarding conductivity relations and possible differences between theory and application. It would have the disadvantage of building upon the errors of individual determinations.

A third and even better method of calibration would be the actual measurement of a large number of samples of known salinity well distributed over the range of the instrument. This was the pro-

² O. Krümmel, *Handbuch der Oceanographie*, Band I, p. 291.

³ A. L. Thuras, *J. Acad. Sci., Washington, D. C.*, 8, p. 685; 1918.

cedure followed by Smith in the calibration of the first two instruments. The calibration of the first bridge, was made in this way during the winter of 1923-24 at the Museum of Comparative Zoölogy, of Harvard University, using about 70 samples whose salinities were determined by titration. These samples had been collected from the North Atlantic during the ice season of 1923, and consequently were particularly well suited for the calibration of this instrument, since they came from the same regions in which the bridge was to be used.

In this calibration the range was so selected that a salinity of 35 ‰ corresponded to a slide-wire reading of 650.3. The resulting calibration curve can be expressed by the equation

$$S = 35 [1 + 293.4 \times 10^{-6} (s - 650.3) + 29.5 \times 10^{-9} (s - 650.3)^2] \quad (8)$$

In order to compare this equation with equation (7) let us put $s' = 650.3$ whence it follows that $n = 1/7,650.3$ and $m = 1/7,349.7$. With these numerical values equation (7) becomes

$$S = 35 [1 + 299.5 \times 10^{-6} (s - 650.3) + 40.7 \times 10^{-9} (s - 650.3)^2] \quad (9)$$

The data on which the constant B (see equation (6)) is based involve differences of 0.0075 reciprocal ohm-cm and, therefore, the uncertainty in the coefficients of equation (9) is 1.3 per cent which means that the first-degree coefficient may be in error by as much as 4×10^{-6} . The difficulty of accurately evaluating the second-degree coefficient of an experimentally determined calibration curve is, in a measure, responsible for the poorer agreement of these coefficients in equations (8) and (9).

There is a further uncertainty arising from the fact that the bridge was out on ice-patrol service for one season after the initial slide-wire test before the calibration was made, and a second slide-wire test made after the second season showed that the lower turn of the slide wire had suffered some corrosion during the intervening two seasons. Bearing in mind the combined uncertainties, equations (8) and (9) show good agreement.

3. PROCEDURE IN USE

Before the apparatus can be used for the determination of the salinity of a number of samples of sea water, preliminary tests and adjustments must be made. These consist of putting into the Y cell a suitable sample of sea water and determining and recording the setting of Q for each of the X cells to be used.

First, all the cells to be used should be filled with sea water of the same, though not necessarily known salinity. Then with any one of the cells used as a Y cell, any other cell used as an X cell, and Q set at about the center of its range, a setting of the index of the slide wire is found at which the bridge is balanced. It should be remembered that in any case a balance of the bridge involves a proper setting of the mutual inductance and of the contact on the Wagner branch. This setting of Q should be recorded; then another cell is used as an X cell and the bridge balanced this time without changing the setting of the slide wire index, but by a change in the setting of Q . In like

manner, a setting of Q , which gives a balance of the bridge for each of the remaining cells used as X cells, is determined and recorded. This serves merely to find the differences in the cell constants and which one of the cells has the lowest resistance when all are filled with sea water of the same salinity.

In case no more cells are available than it is expected will be used at any one time, that cell whose resistance differs most from the average resistance of all may be selected for use as the Y cell, and of the remaining cells that one having the lowest resistance may be used as an X cell in the selection of a sample of sea water of suitable salinity for use in the Y cell. This X cell is then filled with a sample of sea water of definitely known salinity. Assuming the calibration curve or a table giving the readings of the slide-wire index corresponding to different salinities is available, the reading corresponding to the salinity of the sea water in the X cell is found and the slide-wire index set accordingly. By a series of trials a sample of sea water is found for use in the Y cell such that the setting at Q for a balance of the bridge is well toward the lower limit. This may require mixing samples of different salinity or even dilution or concentration. Finally, with the index of the slide wire set to the reading corresponding to the salinity of the sea water to be used as a standard, the X cells are filled with the standard sea water and for each the bridge is balanced by an accurate adjustment of Q . This gives readings of Q for each of the X cells and these must be recorded, since the reading of Q for any one cell must be duplicated whenever it is used in making a measurement. Having the readings of Q which, with the sea water which is in the Y cell, gives with each X cell a reading of the slide-wire index corresponding to that given by the calibration curve for the salinity of the standard, the apparatus should be in readiness for use in making measurements.

In making measurements—

1. Any sea water which may be in X cells is removed by siphoning.
2. Each cell is rinsed with some of the sea water next to be tested in it and then filled with more of this sea water.

3. After the first sample to be tested has come to the temperature of the bath (which usually is about 15 minutes), Q is set at the reading corresponding to the particular X cell, and the bridge accurately balanced by an adjustment of the slide-wire index following the procedure outlined above.

4. The reading of the slide-wire index and any record of the sample which it is desired to keep are recorded.

5. The sea water is removed by siphoning, the cell rinsed, and filled with the sea water next to be tested in it.

6. Another X cell is connected into the bridge in place of the first, and Q set at the reading corresponding to the particular X cell, a similar procedure being followed in making the balance, recording results, emptying, rinsing, and refilling.

7. In like manner, the reading of the slide-wire index is found and recorded for the sample of sea water in each of the remaining X cells, if any.

8. After the second sample placed in the first X cell has come to the temperature of the bath, it may be measured in like manner, and so on until all the samples which may be on hand have been measured.

9. At any convenient time the readings of the slide-wire index may be converted into salinities by reference to the calibration curve or to a table equivalent to the calibration curve.

10. As the salinity of the sea water in the *Y* cell will change with evaporation and condensation, and as the constants of the cells will change with possible variations in the platinum black coating of the electrodes, the readings of *Q* should be checked at the beginning and at the end of each run with samples of standard sea water in each of the *X* cells.

Because of the very large temperature coefficient of electrical conductivity of sea water, it is important that the solutions in the *Y* and *X* cells have the same temperature to within a few thousandths of a degree centigrade when final adjustments for balancing the bridge are made. The previously mentioned feature of design of having two adjacent arms similar in temperature coefficient characteristics makes the actual temperature of relatively small importance, but this is true only where these two arms are subjected to the same temperature conditions. It is therefore necessary for the operator to allow a sufficient length of time for the sample to attain the temperature of the bath after it has been introduced into one of the cells, before measurements can be made with accuracy. Experiments with the first apparatus in 1923 by Smith and with the *Carnegie* instrument in 1928 by Soule indicate that unless the sample introduced is initially close to the temperature of the bath a period of 15 minutes should be allowed for temperature equilibrium to be established.

As the setting of the resistance *Q* is a measure of that part of the sea-water resistance whose temperature coefficient remains uncompensated, it will be seen that it is desirable that all cells used as *X* cells be sufficiently similar that the setting of *Q* for each may be made fairly small.

The accuracy of an individual measurement made with either of the Coast Guard instruments is estimated to be about the same as with titration. That is, the error is within about 0.02 ‰ salinity. However, in the opinion of those who have used both methods, the electrical conductivity apparatus has the advantage that regardless of the violence of the ship's motion the actual measurement is unaffected and the difficulties connected with the handling of liquids under such conditions are much reduced, being restricted to those involved in putting the samples into the cells.

V. CARNEGIE INSTITUTION EQUIPMENT

1. DESCRIPTION

The instrument installed on the *Carnegie* was similar in principle to the first two, but differed somewhat in structural details. A comparison of Figure 7 with Figure 3 will make clear some of these differences. In the *Carnegie* apparatus the electrical switches and controls were mounted on bakelite panels in the upper parts of the two sections. The central partition was retained for the protection of the electrical circuits on the one side in case of accidental spilling of sea water on the other side.

As in the earlier models, the microphone hummer was located in the lower compartment of the left-hand side and surrounded by sound deadening packing. The slide wire was mounted directly above the lower compartment containing the microphone hummer. Mounted

on or back of the left-hand panel were the coils and rheostat for the third arm, the auxiliary resistance Q , the ground switch, the variocoupler for inductive balancing, terminals for the telephone receivers, and a 40-watt incandescent lamp for keeping the humidity low. The switch button for the microphone hummer was placed on the central partition.

On the right-hand panel were mounted the relay for the heater control, the relay rheostat, the stirring motor rheostat, the main supply switch and fuses, a second lamp for drying, and double-pole single-throw switches for the stirring motor, the thermostat, and each of the three X cells. The lower part of the right-hand section was occupied by the water bath, the cover for which served as mounting for the auxiliary cell, the three X cells, the stirring motor and the pump, the mercury thermometer, the thermostat, and the two heating elements. Three X cells were provided instead of the two as used on the earlier instruments in order to reduce the average time necessary for a measurement. The bath was stirred by a small centrifugal fan which was driven by the stirring motor through a disk drive. The thermostat was of a simple, commercially obtainable type having a large mercury well surmounted by a small capillary tube containing two electrical contacts of platinum. The heating elements were also of a type which could be easily purchased. They were of the flat immersion type having a maker's rating of 250 watts each on 110 volts. In order to reduce the rate of heating, the two elements were placed in series. A mounted cell, two thermoregulators, one with and one without its cover removed, and a heating element are shown in Figure 8.

For purposes of electric shielding, the interior of the bridge was copper lined. This shield lining, and other exposed metal parts, were nickel plated to better resist corrosion.

2. CALIBRATION

The time available for the calibration of the *Carnegie* apparatus prior to the departure of the vessel was limited, and, as the calibration of the slide wire as given by the manufacturer showed it to be very uniform, it was accepted without further test as to uniformity. From the experience of the Coast Guard cutters on ice-patrol duty, it had been recommended that the calibration be so selected that the mid-point of the slide wire would correspond to a salinity of about 33.00 ‰. With this recommendation in mind, a rough calculation indicated that the Copenhagen standard water of 34.99 ‰ salinity should correspond to a slide-wire reading of 698.5. This was, therefore, selected as the first and invariable point on the calibration curve. With this point selected as being on the curve by definition, five other samples of known salinity furnished by the Scripps Institution of Oceanography and also titrated by H. R. Seiwel were alternately put into the X cells and the corresponding slide-wire readings determined. From these six well-distributed points a curve was drawn. This gave the data from which was constructed the initial calibration curve which was used to determine the salinity of unknown samples in terms of the Copenhagen standard sea water. From time to time as the cruise progressed some of the samples which were measured in the bridge were also titrated against standard sea water in a Knudsen burette by the silver-nitrate method. Each of these samples furnished

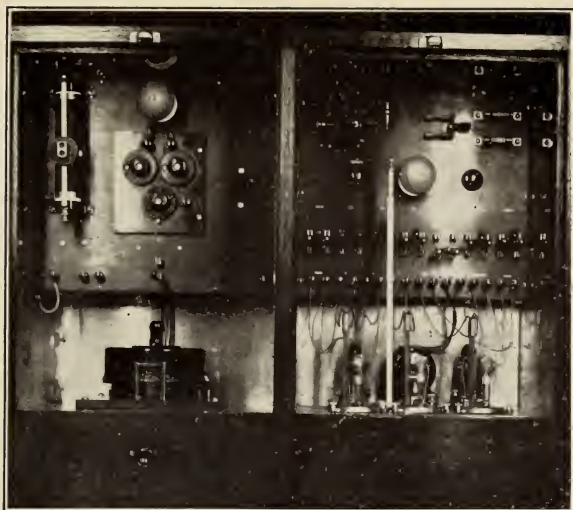


FIGURE 7.—*Carnegie equipment*



FIGURE 8.—*Mounted electrolytic cell, two thermoregulators one with cover removed, and heating element*

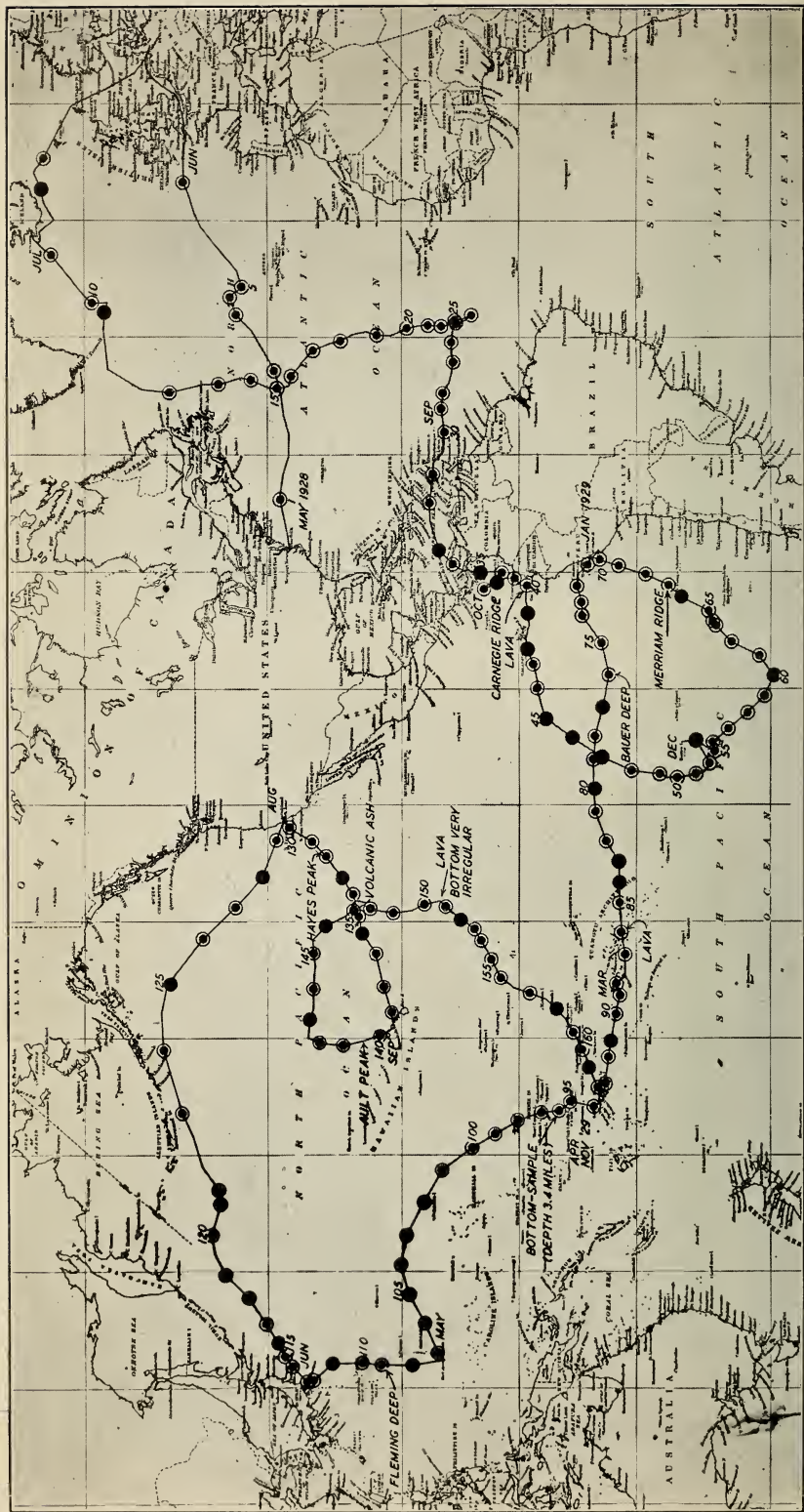


FIGURE 9.—Oceanographic station positions of Carnegie Cruise VII

Arrows point to the locations of the more salient discoveries of the cruise. Total distance covered, 51,800 statute miles.

an additional point on the calibration curve. In all 220 such points, including the arbitrarily selected point, were determined and all used in determining the final calibration curve. Of these, 149 were determined at a temperature of 30° C. and 70 at a temperature of 40° C. Of the points determined at 30° C., 137 were true sea water samples and 12 were prepared or evaporated samples. Of the points determined at 40° C., 68 were true sea water samples and two were prepared samples. The true sea water samples were obtained at 35 different localities widely separated in geographical position, having a latitude range of about 104° from 63° 30' north to 40° 24' south and having a longitude range of about 201° from 14° 41' west to 144° 01' east. The geographical distribution is shown on the chart in Figure 9. The samples used for calibration comparisons were collected at stations indicated by the large dots, the small dots within the circles indicating the stations at which samples were measured but not checked by titration. The points cover a range of depth from the surface down to about 4,000 m. The vertical distribution is shown in Figure 10.

As an individual bridge measurement is accurate to about 0.01 to 0.02 ‰ salinity and as an individual titration measurement is also accurate to about 0.01 to 0.02 ‰, the combined instrumental and observational errors should lead to a scattering of the points of 0.04 ‰ on each side of the curve, representing the relation between salinities and slide-wire index readings. However, as the salinity bridge measures total salt as found, and the titration method measures total halogen salt as found and is corrected for other salt on the assumption that a fixed ratio of salt exists, it was expected that in some localities a considerably greater scatter than 0.04 ‰ on one or the other side of the curve would be found. Actually, though, the scatter is not much greater than that which should have been expected from the errors in titration and bridge measurements, and further there are no systematic differences between the points determined at 30° C. and those determined at 40° C. Therefore, a calibration curve determined at one temperature may be used at another temperature, or at any rate the regulating temperature of the bath need not be adjusted accurately to a specified value.

A calibration curve can be fairly well represented by a second-degree equation of the type

$$S = S_1 [1 + \alpha (s - s_1) + \beta (s - s_1)^2]$$

in which S is the salinity of any sample corresponding to a slide-wire reading of s , S_1 is the salinity of a known sample corresponding to an arbitrarily selected slide-wire reading s_1 , and α and β are numerical coefficients.

For the calibration curve obtained from the 220 titrated samples, the equation is

$$S = 35 [1 + 295.7 \times 10^{-6} (s - 699.5) + 46 \times 10^{-9} (s - 699.5)^2] \quad (10)$$

This can be compared with the theoretical equation (7) by equating s' to 699.5 from which it follows that $n = 1/7,699.5$ and $m = 1/7,399.5$, and equation (7) becomes

$$S = 35 [1 + 299.6 \times 10^{-6} (s - 699.5) + 41.1 \times 10^{-9} (s - 699.5)^2] \quad (11)$$

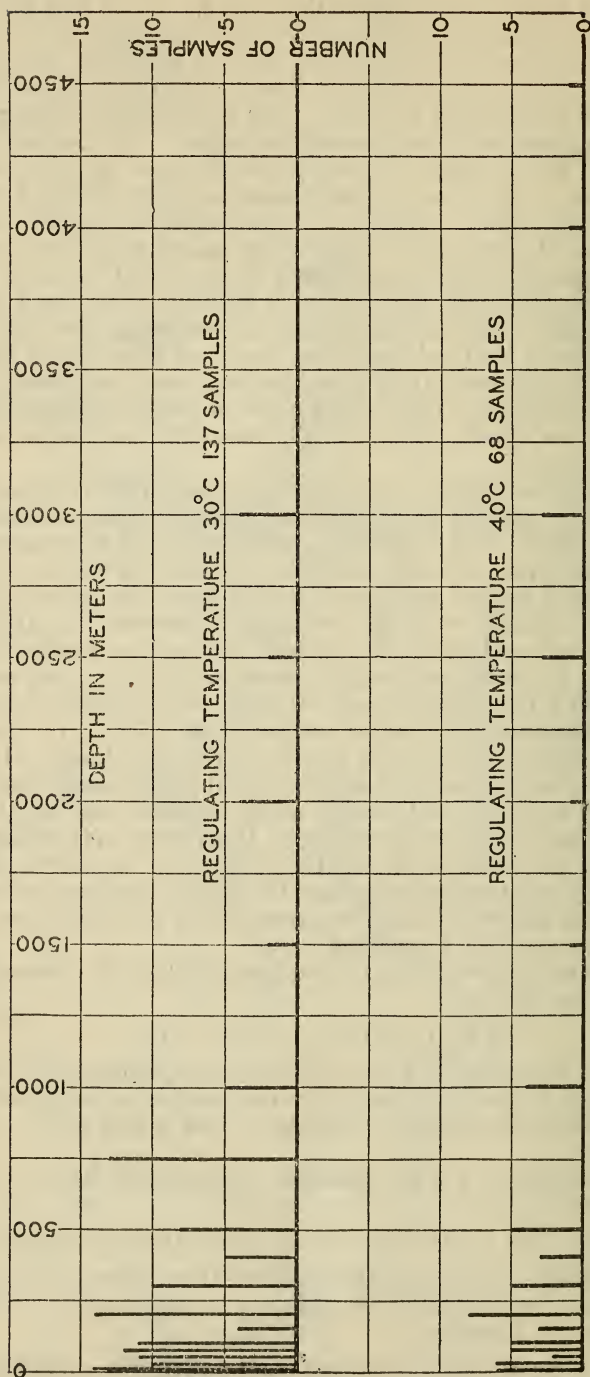


FIGURE 10.—Vertical distribution of calibration samples used in Carnegie equipment

The agreement between equations (10) and (11) is good considering again the previously discussed uncertainty of 4×10^{-6} in the first-degree coefficient of the theoretical equation.

In the development of the theoretical equation it has been assumed that the resistance in the *X* arm of the bridge is made up entirely of the resistance of the solution in the *X* cell. Actually, of course, there is some small fixed resistance embodied in the cell terminals and leads. A generous estimate of this fixed resistance would be 0.1 per cent of the resistance of the *X* arm, or about 0.2 ohm. If such were the case the first-degree coefficient would only be changed by about 0.3×10^{-6} and the second-degree coefficient would only be changed by about 0.1×10^{-9} . In view of the other uncertainties, it is justifiable to neglect this fixed resistance.

The experimental results obtained on the *Carnegie* differ most from the second-degree equation in the vicinity of slide wire reading equal to 800. Here a number of points fall above the curve of the equation. This may have been caused by a lack of uniformity in that part of the slide wire, although this is not indicated by the manufacturer's report. About a dozen of the outstanding departures from this part of the curve were investigated as to geographical origin. Two were found to have been evaporated or prepared samples, and the other ten which were true sea-water samples came from the upper 200 m of stations No. 46, 47, 91, and 161. Curiously enough, these stations all have about the same latitude (between 9° south and 16° south), while their longitudes vary from that of Easter Island to that of the Samoan Islands. Although the coincidence is suggestive, no conclusions regarding salt ratios can be drawn since these data are far too meager.

Other systematic deviations from the second-degree equation occur, but have no apparent relation to geographical position. One can assume that such deviations are caused either by lack of uniformity in the slide wire or by variation in composition of the salt. However, if the latter assumption is made, it requires that the composition be an irregular function of the salinity. Such a relationship seems highly improbable. In view of these considerations and the above discussion of the theoretical form of an equation for the calibration curve, the bridge measurements made on the *Carnegie* were converted into salinities by the use of the second-degree equation given, and a table of corrections based on systematic variations of the titration comparisons from that curve. When such corrections are applied to the second-degree equation, 212 out of the 219 titration comparisons fall within a difference of 0.04 ‰ . This seems to show an even greater constancy of salt composition than has been assumed in the past and leads one to question the accuracy of chemical analyses of sea water as published in the past. Such published analyses indicate that if solutions of each were adjusted to equal concentration the salinities as given by titration would differ in some cases in the first decimal place of parts per thousand. Obviously no such variations were encountered in the cruise of the *Carnegie*.

The authors are not aware of the existence of data on the variation of conductivity of sea water of constant concentration with variation in composition. Since the ratio of mobility to weight of

the constituent ions differs, it is true that the conductivity will not be independent of the composition. However, there are many kinds of ions present, and as dissociation is never complete, the complexity of the problem precludes an accurate quantitative theoretical analysis and one can only say that the variation in conductivity is small and probably the conductivity method comes closest, of available field methods, to the measurement of total salt.

3. DISCUSSION OF TEMPERATURE COEFFICIENT

The previously mentioned design feature of having similar electrolytic cells form two adjacent arms of the bridge has, as one of its objectives, lessening the importance of accurate temperature control. In other words, it was hoped that by this device the effective temperature coefficient of the instrument would be very much less than that of sea water. The efficacy of this arrangement was tested on the *Carnegie* as follows: When the regulating temperature of the water bath was changed from 30° to 40° C., Copenhagen standard water, which was used as the final standard at the end of the last 30° C. routine salinity run, was left in the cells and was remeasured on the following day at 40° C., with the auxiliary resistance Q having the same setting as was used at 30° C. The differences in slide-wire readings were converted into differences in salinity and considered to be the effect produced by a 10° C. change in temperature of a sample. This was done on a basis of 1.0 unit on the slide wire corresponding to a change of 0.01 ‰ in salinity. This procedure further was based on the assumptions that during the period of about 24 hours the salinity of the solution in the auxiliary or Y cell did not change and that the cell constants did not change. Such assumptions were justifiable as only a rough determination was made. The slide-wire reading at the balance of the initial standard was 698.5 in each case, by definition. Either because of changes in cell constants or changes on the auxiliary cell solutions, the slide-wire readings were slightly different for the final standard than for the initial standard. If it is assumed that these changes were permanent, the slide-wire readings for the final standard should be used, whereas if these changes are assumed to have been temporary and to have disappeared (such as might be the case if part of the auxiliary cell solution vaporized during the run and condensed again afterward), then the slide-wire readings of the final standard should be used. Following the remeasurement of the final standards at 40° C., they were withdrawn and replaced by other samples, originally having the same salinity, and another series of slide-wire readings taken. Assuming that no change in salinity of the final standards had occurred, the final standard as remeasured should be used. If it be assumed that the final standard had changed in salinity, then the fresh standard should be used. Thus there are four combinations per cell which will give a temperature coefficient of salinity. Their means have been taken as shown in Table 1.

TABLE 1.—Data for temperature coefficients of salinity for cells A, B, and C

Cell	Observation	Temperature	Standard	Q	Slide-wire reading	Temperature coefficient	
						From—	Value
A	I	30	Initial	1.913	698.5	I and III	$\frac{1}{100}$ per ° C.
	II	30	Final	1.913	698.1	I and IV	0.0073
	III	40	do	1.913	706.3	II and III	47
	IV	40	New	1.913	703.2	II and IV	82
							51
Mean for cell A.							.0064
B	I	30	Initial	3.048	698.5	I and III	.0041
	II	30	Final	3.048	698.2	I and IV	67
	III	40	do	3.048	702.6	II and III	44
	IV	40	New	3.048	705.2	II and IV	70
Mean for cell B.							.0056
C	I	30	Initial	3.208	698.5	I and III	.0138
	II	30	Final	3.208	698.7	I and IV	116
	III	40	do	3.208	712.3	II and III	136
	IV	40	New	3.208	710.1	II and IV	114
Mean for cell C.							.0126

These temperature coefficients, even if accurately determined, would only apply with the same settings of the auxiliary resistance Q . As the settings given above approximately represent ohms and as the resistance of the cells were about 250 to 300 ohms each, it is seen that the uncompensated sea-water resistance was about 1 per cent of the resistance of the unknown. Taking the temperature coefficient of electrical conductivity of sea water as 3 per cent per degree centigrade, the temperature coefficient of salinity of the bridge would have been expected to be of the order of 0.0003×35.00 or about $0.01 \frac{1}{100}$ per degree centigrade. The general agreement between the experimental and calculated values indicates that the temperature coefficient of the bridge arm containing the Y cell differed from that of the arm containing the X cell by not more than 3 parts in 10,000. This would not be true generally, but would depend upon the difference in cell constants of the X and Y cells and upon the ratio of the resistance of Q to the resistance of the sea water in the Y cell. It may be noted, however, that had a wire resistance been used in place of sea water in the Y cell, the temperature coefficient would have been in the neighborhood of 0.03×35 or about $1 \frac{1}{100}$ per degree centigrade. It should be understood that the wire resistances in the bridge were of manganin, having a negligible temperature coefficient, and that when measurements were made the X and Y cells were accurately at the same temperature.

VI. RECOMMENDED CHANGES IN CONSTRUCTION

Practical experience with the salinity bridges under actual field conditions suggests that the instrument might be improved somewhat by making a few minor changes. The following recommendations regarding future construction are therefore made.

In a multiple X cell bridge (that is, one having more than one cell for unknown solutions) it is necessary to change the setting of the auxiliary resistance Q from one value to another as the different cells are used. It therefore is necessary, when returning to a given X cell, to be able to duplicate not only the original setting of Q corresponding to that particular cell, but also to have the resistance indicated by that setting the same as the resistance for the original setting. The uncertainty of any measurement will hence be affected if the resistance of the auxiliary switch contacts is uncertain. While it would take an uncertainty in contact resistance of nearly 0.1 ohm to produce an uncertainty in the measurement of about 0.01 % salinity, and while it is easily possible to keep the uncertainty in switch contacts below this figure, it is also true that a defective switch or one of poor construction can develop such an uncertainty. Good workmanship is important in the construction of these switches. A recommended design is one in which the total resistance is soldered into the circuit and individual coils are successively short circuited by a multiple spring-leaf dial switch having double diametrical segment contacts. Such an arrangement places two contacts in parallel and, as it is improbable that both contacts will become defective simultaneously, the chance of troublesome switch contacts is thereby reduced. Even with good design and workmanship, the switches of the auxiliary resistance should occasionally be inspected and tested for uncertainty of resistance. The constancy of the switch contact resistances is improved if the contacts are kept lubricated with clean oil.

The size of the electrolytic cells might well be reduced to half the dimensions used in the first three instruments. This would reduce the volume to about one-quarter and would not only mean a saving in standard water, but would leave more of the unknown sample for other determinations. A small saving would result from the reduced size of the electrodes. The resistance of the cell would be about doubled, thus reducing the importance of contact resistances. Less space would be needed per cell in the water bath, and possibly less time would be required for the sample to come to the regulating temperature. If the voltage of the test current supply is kept the same, the heat produced by the test current per cell will be halved and, as the rate of dissipation of this heat would probably not be as much affected, the test current would probably have a smaller effect on the temperature of the sample. It is realized that greater care would be necessary in the manufacture of the smaller cells, but it is believed that the advantages to be gained make the change desirable.

As it was estimated that 15 minutes were required for a sample to reach the temperature of the water bath under conditions of low room temperature, and as about two minutes are required for measurement, rinsing, and refilling, it seems best to have six X cells. The number of samples to be measured per run will determine to some extent the optimum number of cells.

It is probable that the test current dissipated about 0.005 watt per cell and for future construction it is recommended that the test current be reduced to one-half, or less, of that previously used. The resulting loss in sensitivity would be more than counterbalanced by the use of telephone receivers tuned to the frequency of the test current; that is, 1,000 cycles. They should still, of course, be selected

to have about the same impedance as the bridge arms. The tuning should be done at the factory or in the laboratory and should not be adjustable, as unnecessary adjustments are undesirable in any field instrument.

Even with careful construction certain inspections should be made from time to time and minor repairs may be necessary in the field. All circuits should therefore be made accessible, even though ordinarily protected. Hence, ample doors or removable covers should be placed in the case of the instrument back of the panels.

The range of salinities covered by the bridge will be governed largely by the purpose to which it is to be put, and by the nature of the expedition which will use it. If measurements are to be made in in-shore waters, or in the vicinities of the mouths of large rivers, a lower limit of 28 ‰ salinity or less should be selected. However, if measurements are to be made chiefly in the open seas, the lower limit should be at least 30 ‰. This would give an upper limit of about 40 ‰. A point to be remembered in selecting the salinity range is that that portion of the range which is below the salinities actually encountered at sea is wasted, whereas that portion which is above the salinities found in the sea can be used in evaporation work. It might be advisable to calibrate an instrument for two overlapping ranges. If such a procedure is followed it should be remembered that the deep water in most ocean areas is between 34.50 and 35.00 ‰ in salinity. It would be well, therefore, to include this in the overlap. Recommended ranges are 25.25 ‰ to 35.25 ‰ and 33.50 ‰ to 43.50 ‰. In this recommendation the lower limit of the upper range and upper limit of the lower range are stressed, the other two limits being given merely to indicate the approximate total range of the calibrations. The transfer from one range to another may be accomplished by changing only the concentration of the solution in the auxiliary cell. However, if such a change is to be made frequently, much time will be saved by having two *Y* cells, either of which may be switched into the circuit, rather than actually changing the solution in a single *Y* cell.

A warning should be given that a calibration curve can not be shifted parallel to itself without introducing errors. These errors arise from the fact that a change of one division of the slide-wire reading at balance means a change of resistance of about $2/7,500$ at the middle of the slide wire, whereas at the end of the slide wire the same change in setting means a change in resistance of $1/7,000$ plus $1/8,000$. Differently expressed, the middle 250 divisions of the slide wire correspond to a change in salinity which is about 0.3 ‰ more than the change in salinity corresponding to the lower 250 divisions of the slide wire. It will be seen, then, that in the case of two overlapping ranges, calibration points on the overlap determined on one of the ranges can not be transferred to the other range by a constant displacement, but must be determined by actual measurement on both ranges.

VII. SUMMARY

The electrical salinity bridge described was the result of the oceanographic demands of the International Ice Patrol in the North Atlantic Ocean.

An accurate and rugged instrument suited to severe sea conditions was developed, and instruments built and used with satisfactory results.

The instrument as described compares well in performance with titration measurements, is capable of individual measurements accurate to within $0.02^{\circ}/_{\text{oo}}$, and is well adapted to the measurement of total salt.

The temperature compensation has been tested and found to be effective and in agreement with the results expected from theory.

The calibrations of actual instruments have been compared and can be fairly well predicted for similar instruments built in the future.

Experience with the first three instruments built has led to the recommendation of several changes in details of construction considered to be improvements over the first models.

WASHINGTON, June 17, 1930.

